Destruction of disinfection byproducts and their precursors in swimming pool water by combined UV treatment and ozonation

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#12 - Byproduct Formation and Control

Destruction of disinfection byproducts and their precursors in swimming pool water by combined UV treatment and ozonation

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Abstract
Both UV treatment and ozonation are used to reduce different types of disinfection byproducts (DBP) in swimming pools. UV treatment is most common as it is particularly efficient in removing the repulsive chlorine like smelling chloramines (combined chlorine). UV treatment of a pool water increased chlorine reactivity and formation of chlor-organic DBP such as trihalomethanes. Based on the similar selective reactivity of ozone and chlorine we hypothesized that the created reactivity towards chlorine by UV treatment of dissolved organic matter in pool water might also be expressed as an increased reactivity towards ozone and that ozonation might saturate the chlorine reactivity created by UV treatment and mitigate the increased DBP formation. By experimentally treating pool water samples, we found that UV treatment makes pool water highly reactive to ozone. The created reactivity towards chlorine decreases dose dependently with ozone dosage prior to contact with chlorine. Furthermore, the kinetics of ozone in UV treated pool water changed drastically from a half-life in excess of 20 min to complete consumption in less than 2 min. We discovered that ozonation in UV treated pool water induced formation of some DBPs that are not commonly reported in pool water where trichloronitromethane is noteworthy as it is genotoxic. Therefore, we performed repeated treatment experiments consisting of combined UV/ozone treatment interchanged with chlorination for 24 h the genotoxicity created during the ozone treatment was removed by the UV treatments. Based on the experimental results, a treatment system is proposed with a UV system placed in a side stream to the recirculation flow followed by an ozone dosing point and a small reaction chamber with a volume that allow 1-2 min reaction time before returning to the main recirculation flow. This side-stream UV/ozone treatment will improve the swimming pool water quality.

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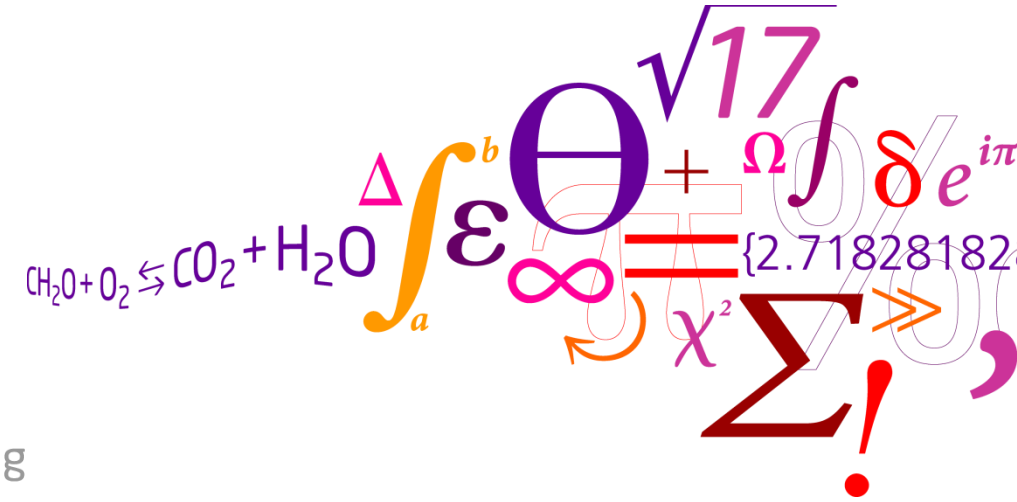
Vancouver, British Columbia,
Canada



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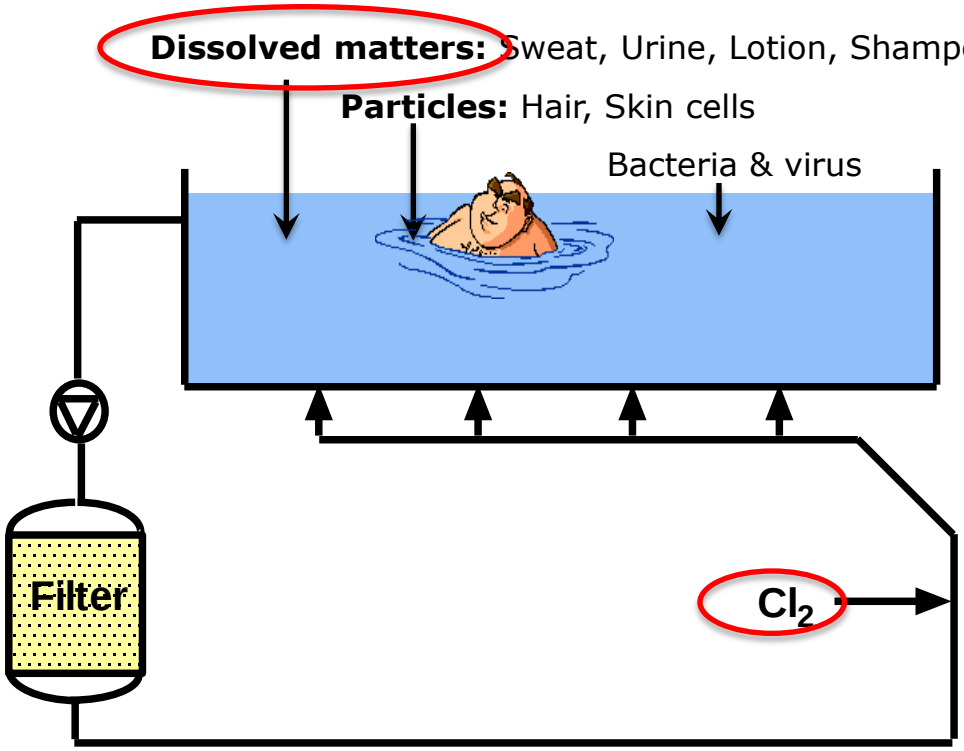
Conventional treatments
Disinfection By-Products



Chlorine + Dissolved Matter

↓

Disinfection By-Products (DBPs)

Inorganic e.g. Chloramines

Organic e.g. Trihalomethanes (THMs)
Haloacetonitriles (HANs)
Haloacetic acids (HAAs)

Disinfection By-Products

	Compound	Abbreviation	Chemical structure
Trihalomethanes (THMs)	Chloroform	TCM	$CHCl_3$
	Bromodichloromethane	BDCM	$CHBrCl_2$
	Dibromochloromethane	DBCM	$CHBr_2Cl$
	Bromoform	TBM	$CHBr_3$
Haloacetonitriles (HANs)	Dichloroacetonitrile	DCAN	CHCl2CN
	Bromochloroacetanotile	BCAN	CHBrClCN
Miscellaneous	Trichloronitromethane	TCnitro	CCl3NO2
	Dichloropropanone	DCprop	CHCl2COCH3
	Trichloropropanone	TCprop	CCl3COCH3

Toxicity estimation

- The toxicity of the different groups

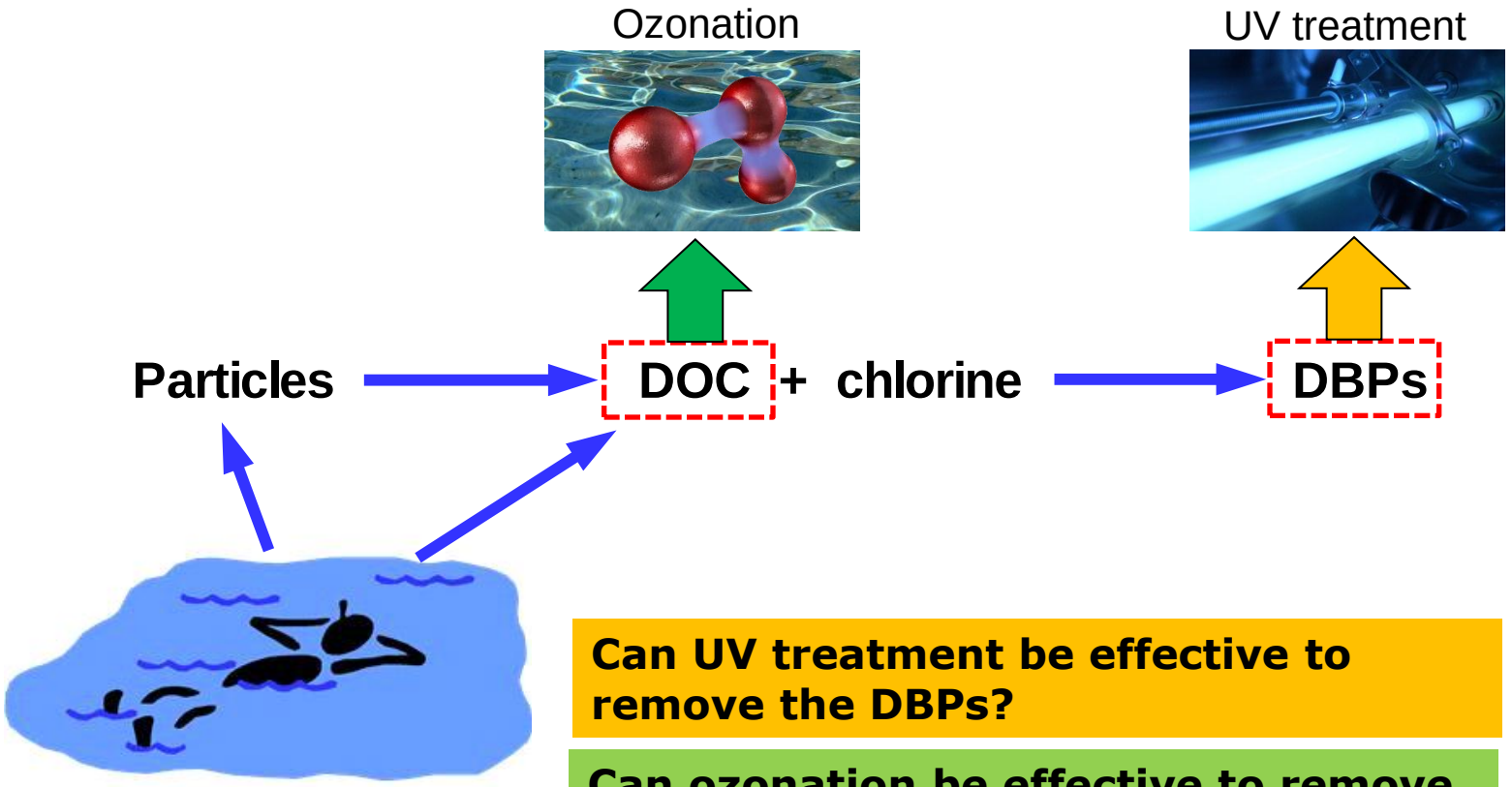
  Haloacetonitriles (HANs) > Haloacetic acids (HAAs) > Trihalomethanes (THMs)

- Calculated for water samples by:

$$Toxicity = \sum \frac{C_i}{EC_{50,i}}$$

- EC_{50} taken from Plewa et al. 2008

Emerging treatment technologies

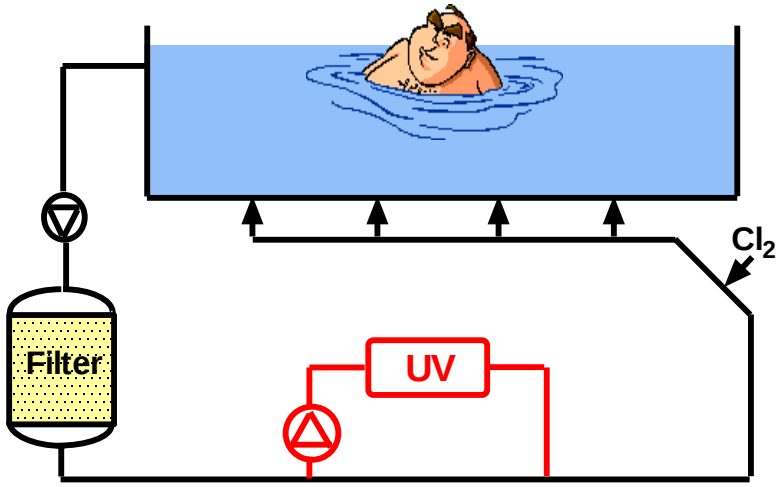


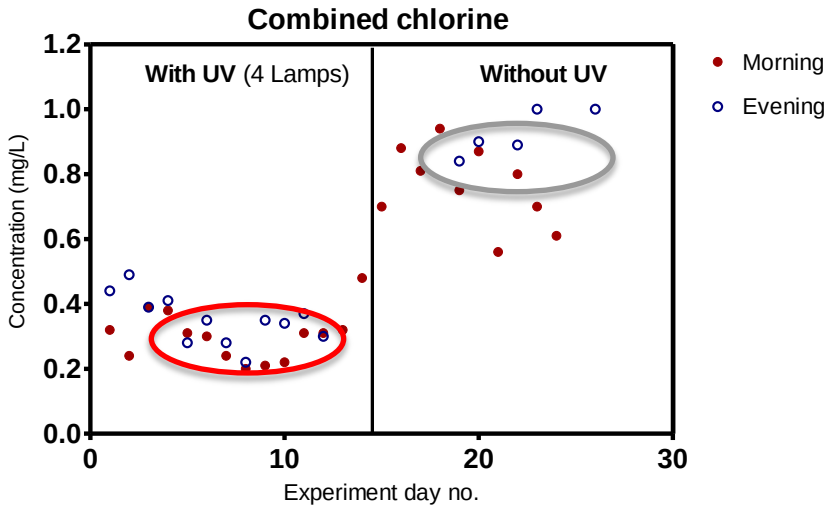
Can UV treatment be effective to remove the DBPs?

Can ozonation be effective to remove reactivity of organic matter towards chlorine?

UV treatment

Advantage (established)
- UV treatment followed by Cl_2 → decreased combined Cl_2





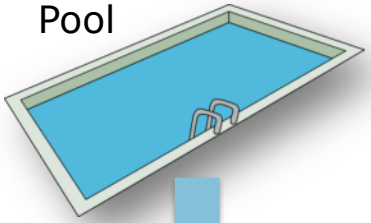
Kristensen et al., 2010

Disadvantage (still need to be established)
- UV treatment followed by Cl_2 → Increased chloro-organic byproducts

Experimental setup

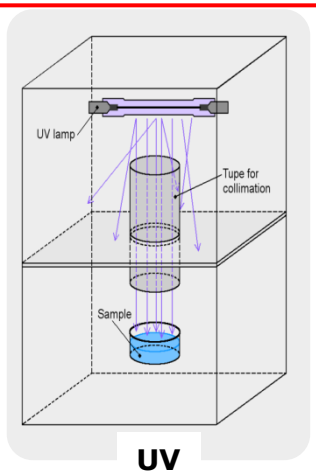
Sampling

Swimming Pool



Water samples

Treatment



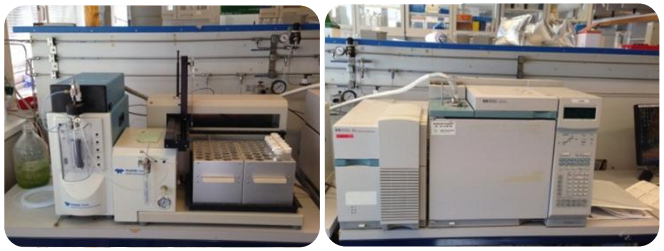
UV

24 hr
25 °C

Residual Chlorine
1±0.3 mg/L

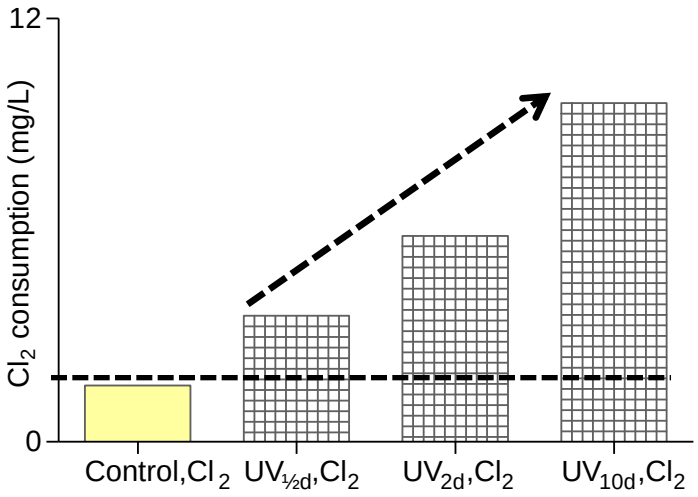
Analysis

Purge & trap
GC/MS

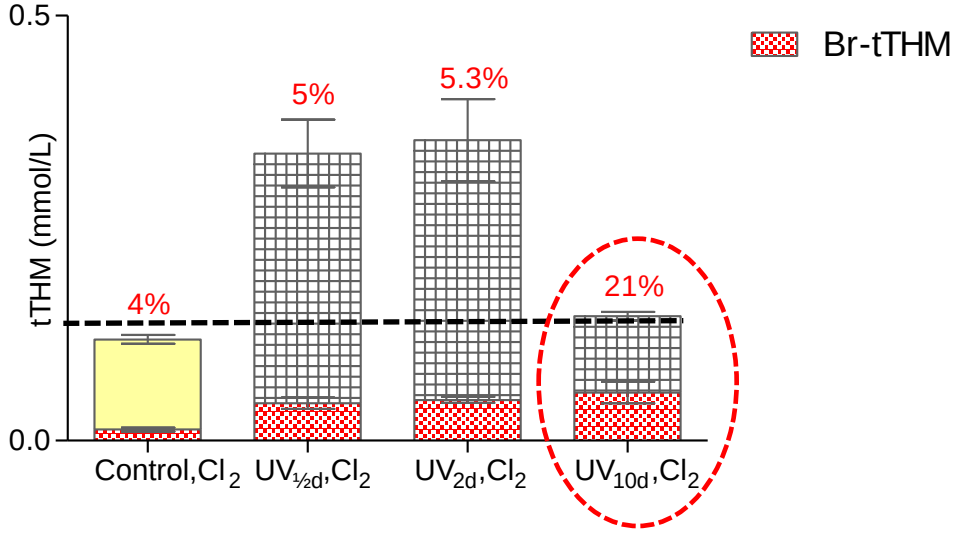


Results

Cl_2 consumption

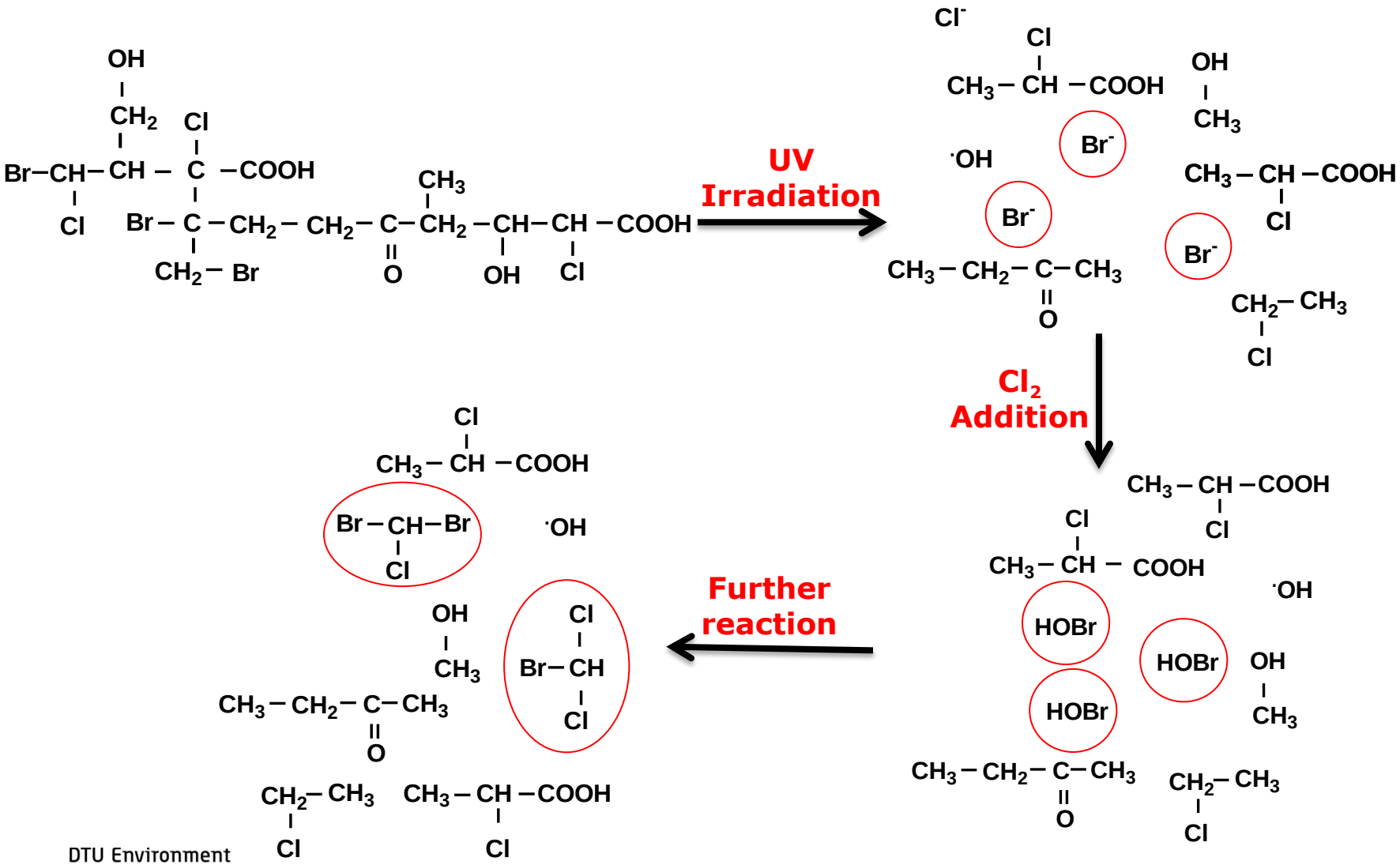


Total Trihalomethane



- UV treatment followed by Cl_2 → increased Cl_2 reactivity
- Increasing UV dose followed by Cl_2 → no effect on Total THMs
- Increasing UV dose followed by Cl_2 → increased Br-THMs

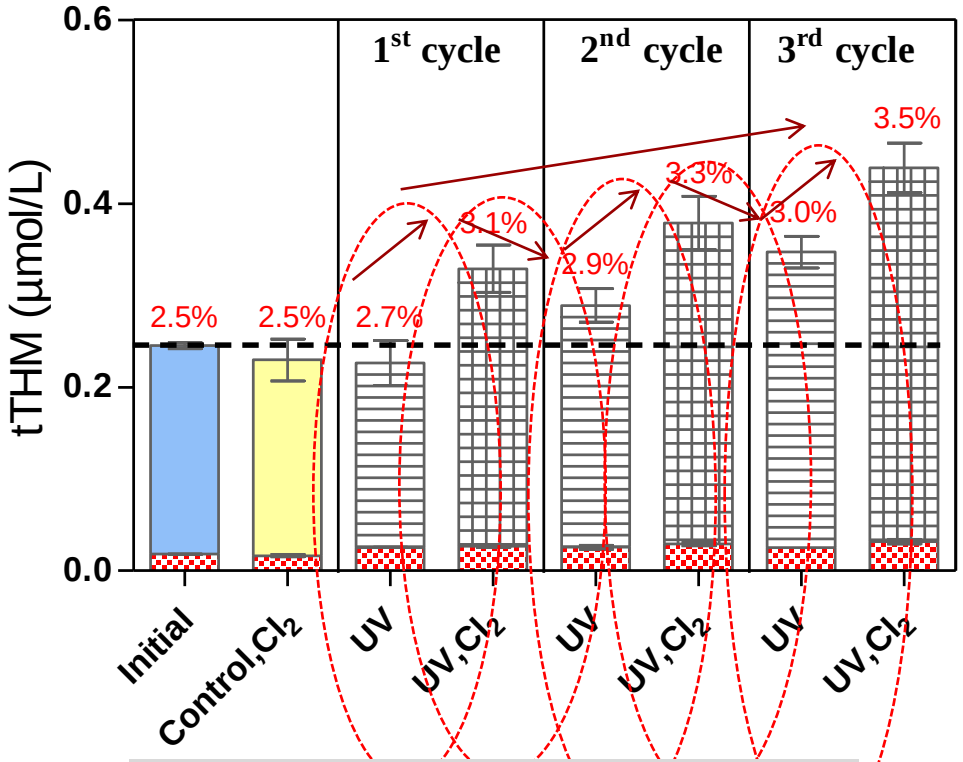
Br-Cl-DBP Formation Theory



Spiliotopoulou et al., (2015)

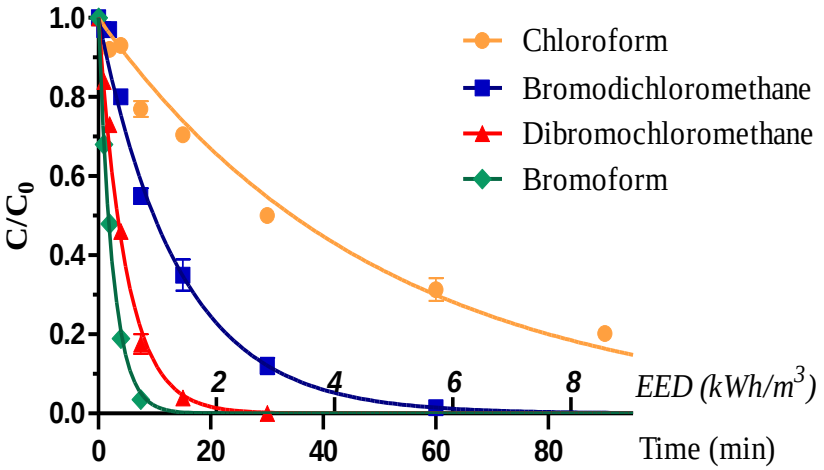
Effect of repeated treatments

Total Trihalomethane



- UV treatment followed by Cl_2 → increased total THM
- UV treatment → decreased total THM

UV photolysis



Hansen et al., (2013)

- Increased bromine substitution → increasing UV photolysis

Ozone in pools

Oxidation of pollutants

I. Direct reaction

$$DOC + O_3 \rightarrow DOC_{selectively\ oxidized}$$

- Fast consumption of ozone
- Decrease chlorine reactivity of pollutants
- Low ozone life time → no reaction with bromide

II. Radical reaction

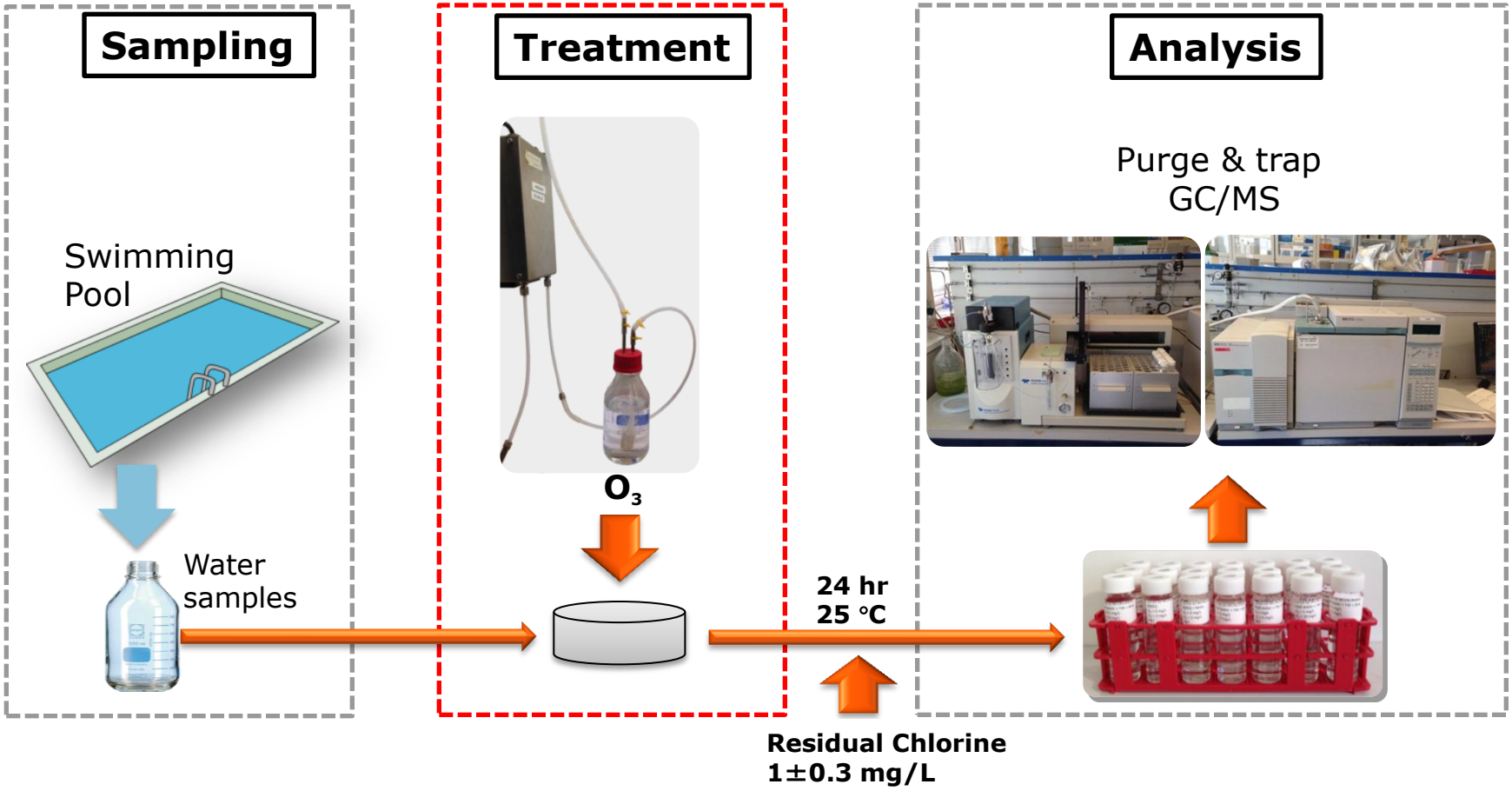
$$H_2O + O_3 \rightarrow O_2 + 2\ HO^{\bullet}$$

$$DOC + HO^{\bullet} \rightarrow DOC_{radical\ oxidized}$$

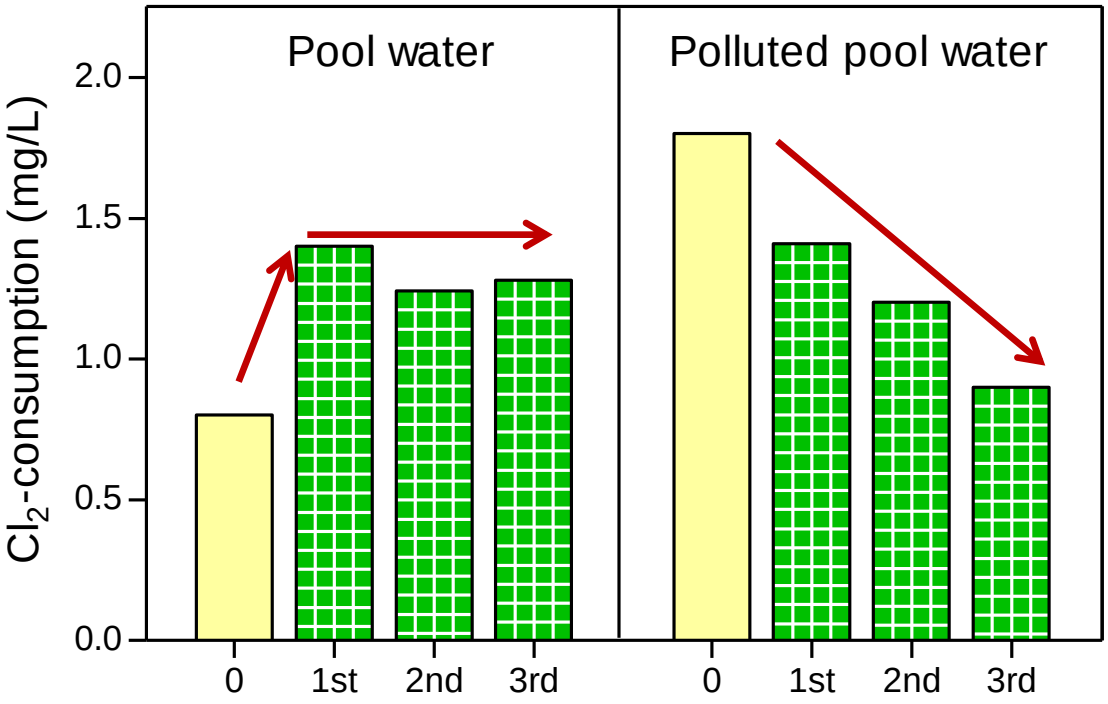
- Slow consumption of ozone
- Ozone converts to hydroxyl radicals with time
- Radical attack of inactive carbon → increased chlorine reactivity
- Long ozone life time → oxidation of bromide to bromate

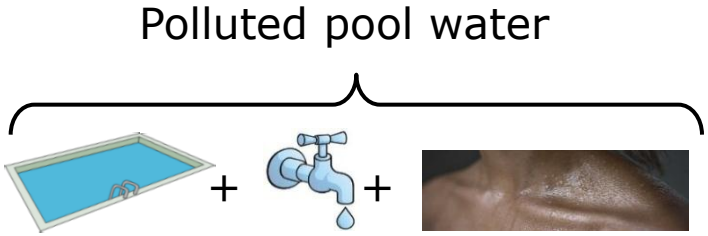
Hansen et al.,(2016)

Experimental setup



Cl_2 consumption

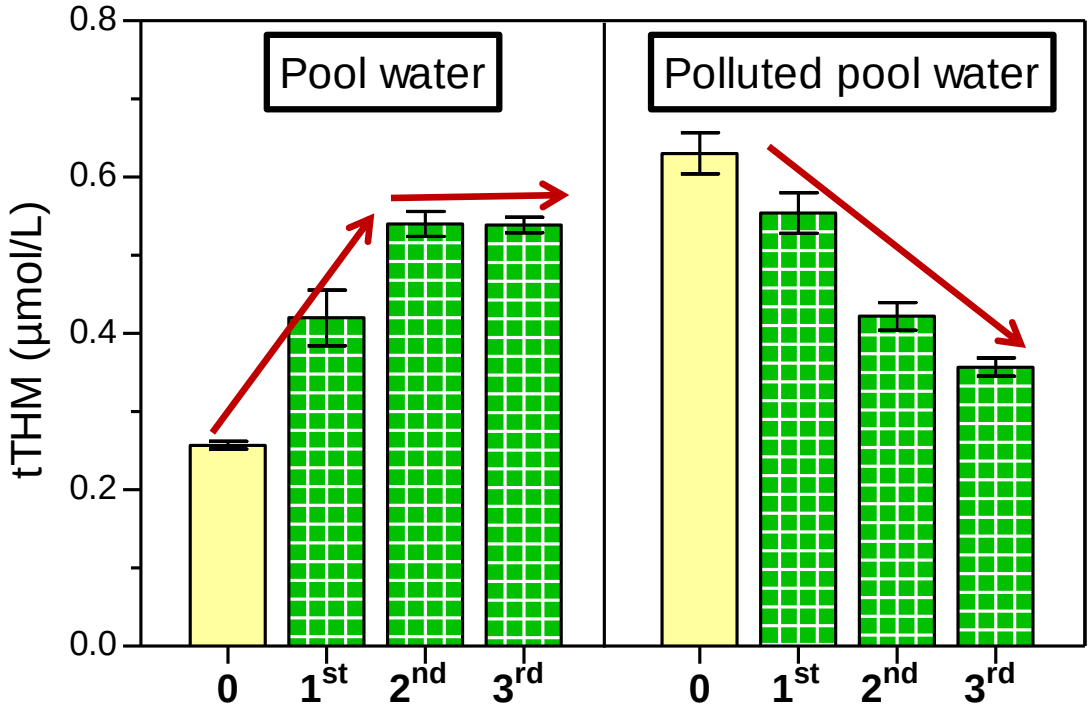




- Ozonation of pool water → increased Cl_2 reactivity
- Ozonation of polluted pool water → decreased Cl_2 reactivity

Hansen et al.,(2016)

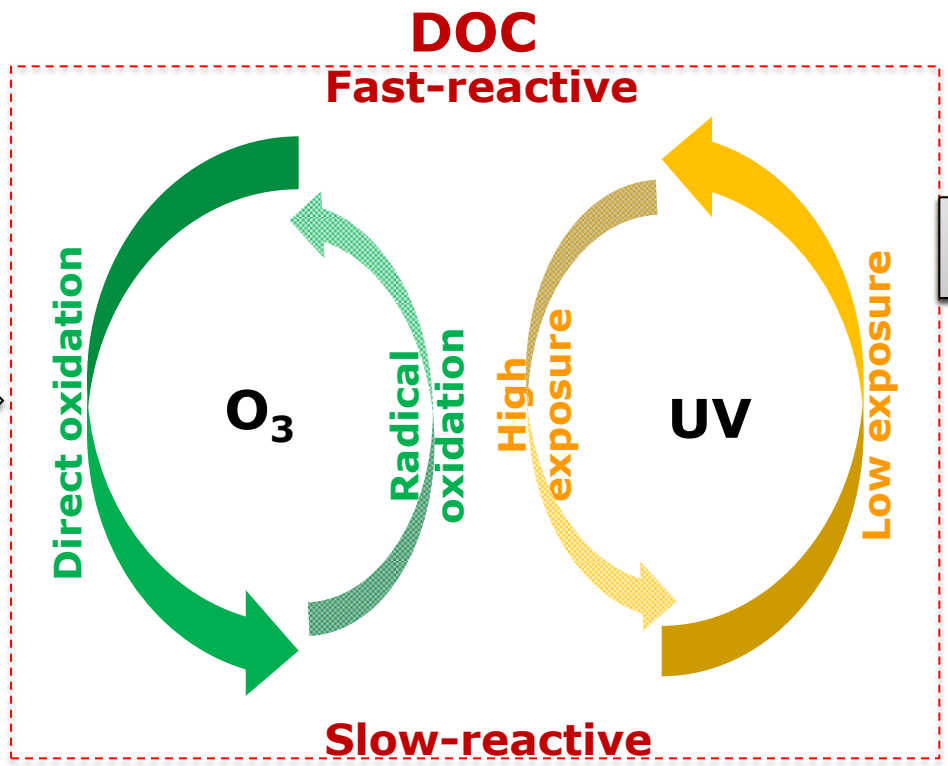
Total Trihalomethane



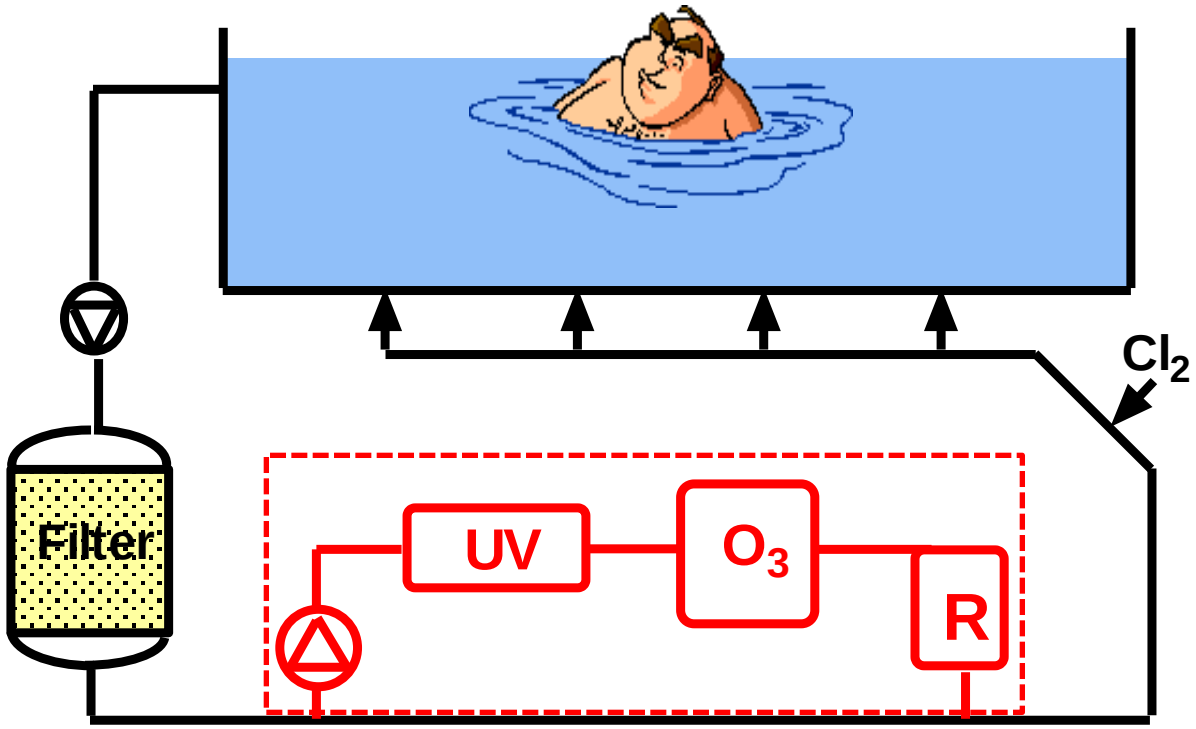
- Ozonation of pool water → increased total THM
- Ozonation of polluted pool water → decreased total THM
- Polluted pool water direct ozone reaction → short ozone life time

Hansen et al.,(2016)

UV and ozone treatments
Summary



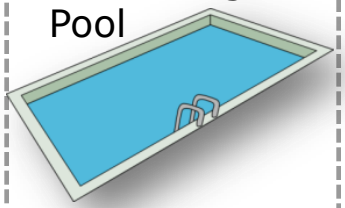
Proposed system design



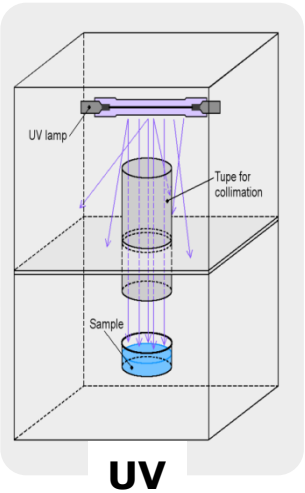
Experimental setup

Sampling **Treatment** **Analysis**

Swimming Pool



Water samples



UV

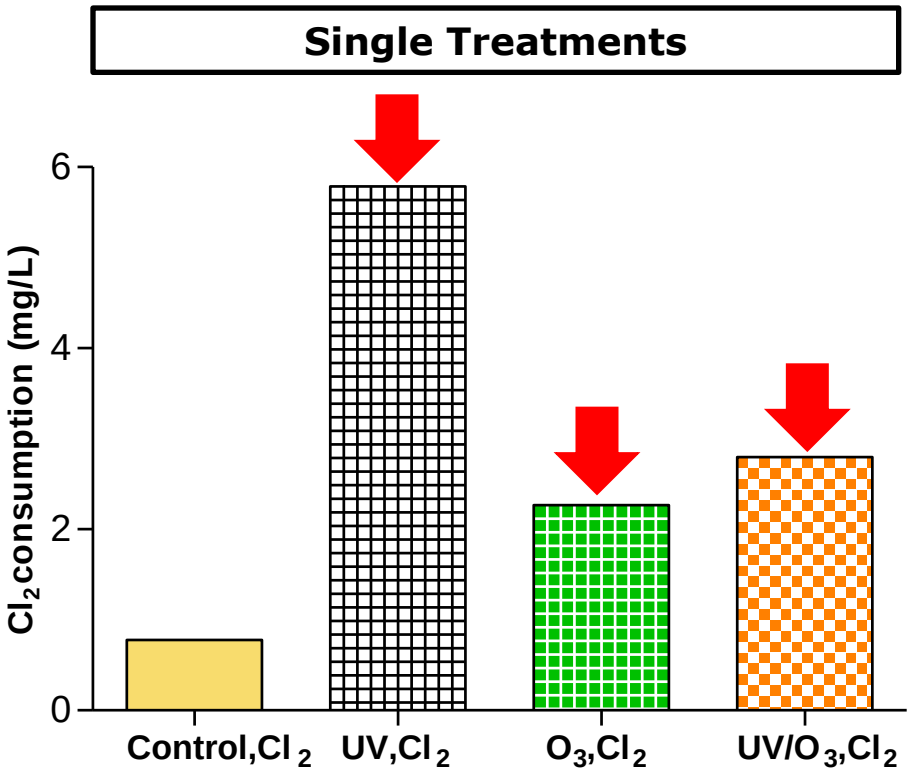
O_3

24 hr
25 °C

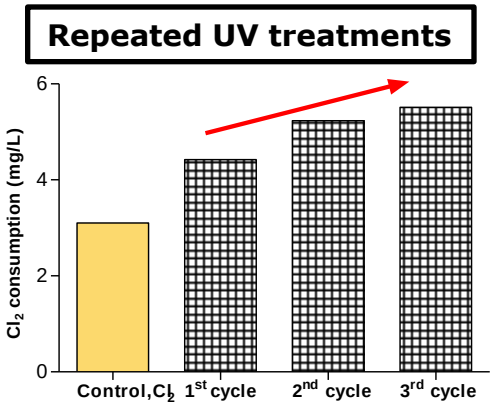
Residual Chlorine
1±0.3 mg/L

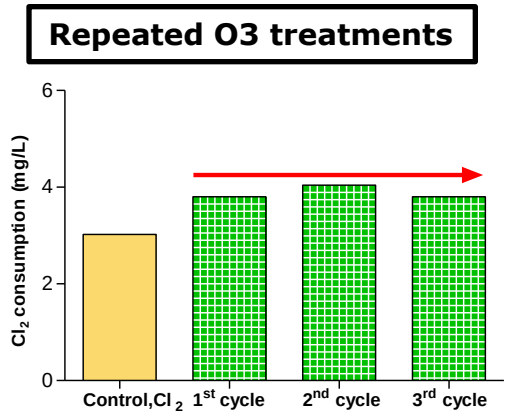
Purge & trap GC/MS

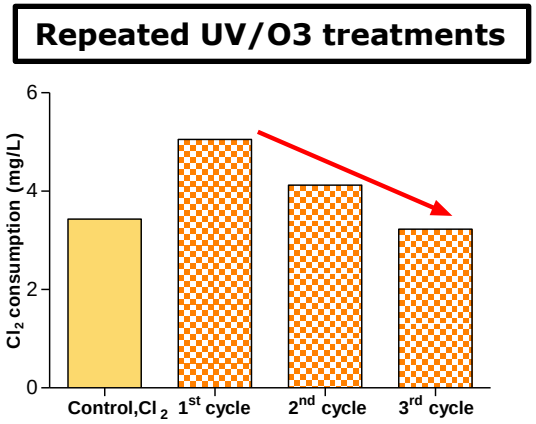
Cl_2 consumption



- Repeated UV treatments increased Cl_2 consumption
- Repeated O_3 treatments had no effect on Cl_2 consumption
- Repeated UV/O_3 treatments decreased Cl_2 consumption







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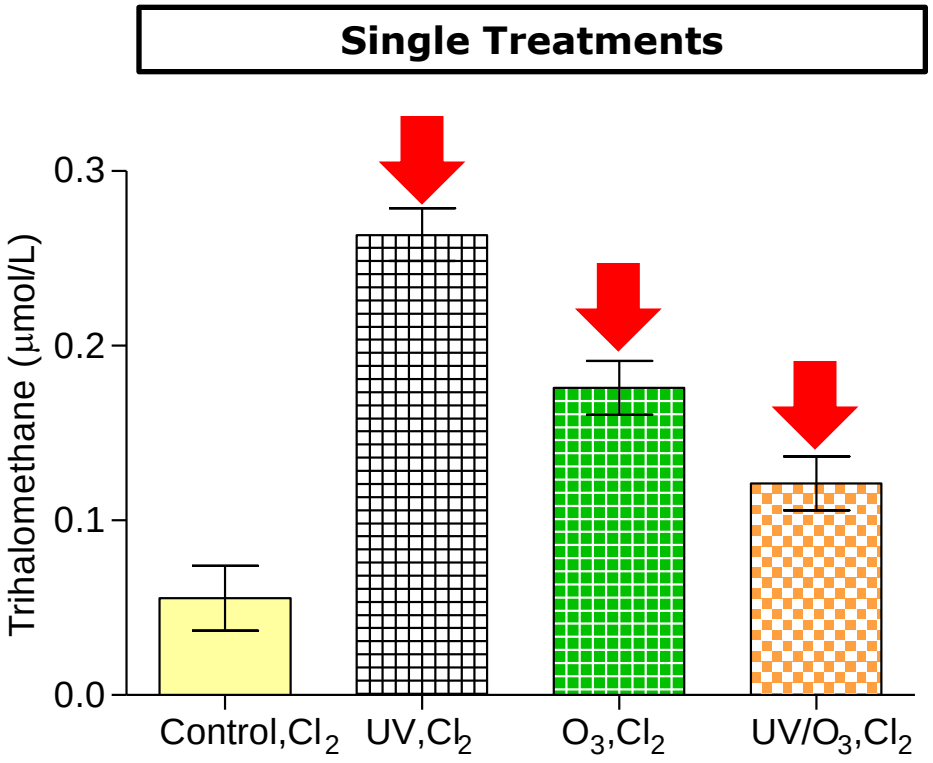
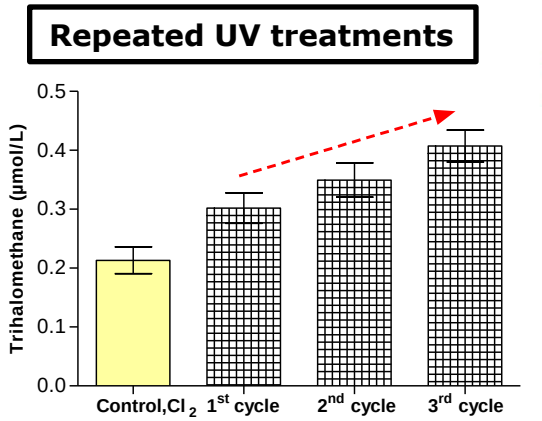
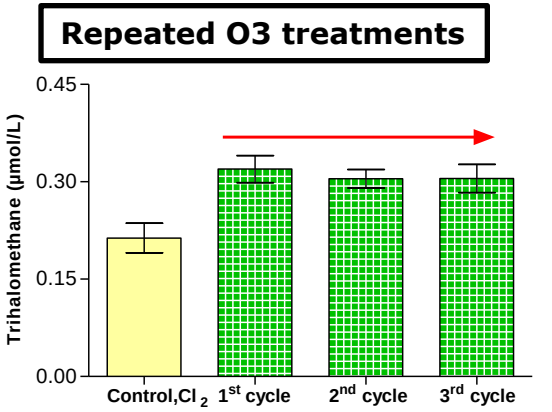
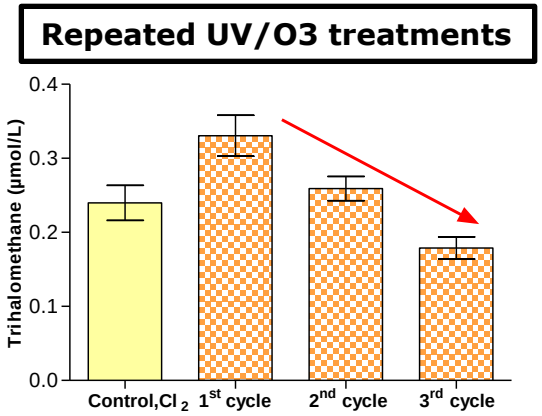
Total Trihalomethane





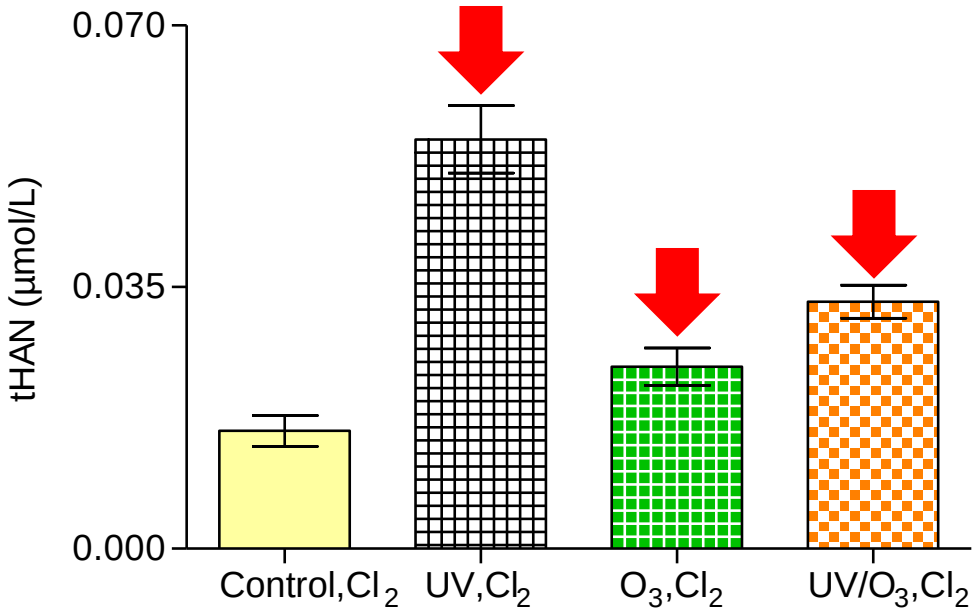




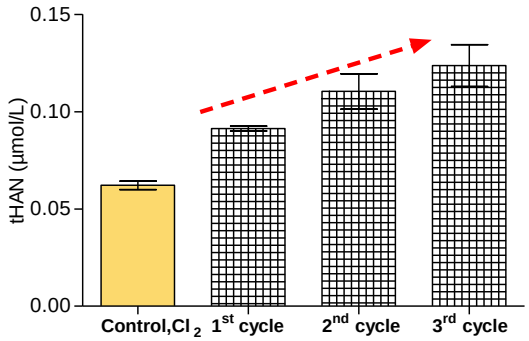
- Repeated UV treatments increased THM concentration
- Repeated O_3 treatments had no effect on THM concentration
- Repeated UV/O_3 treatments decreased THM concentration

Total Haloacetonitrile

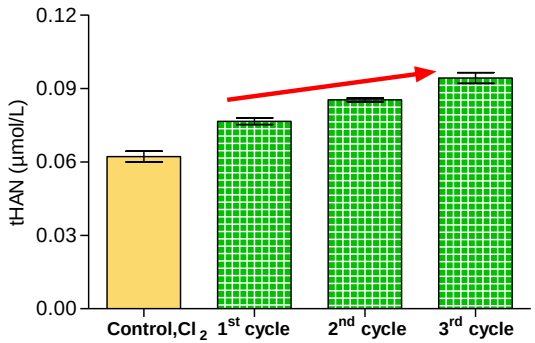
Single Treatments



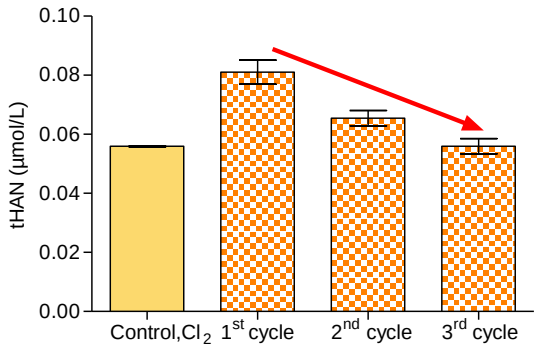
Repeated UV treatments



Repeated O3 treatments



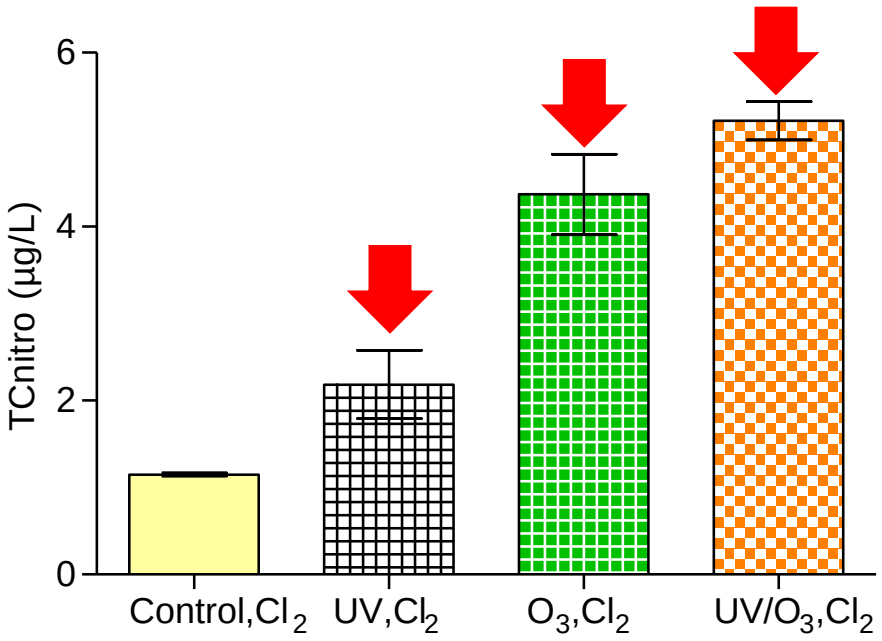
Repeated UV/O3 treatments



- Repeated UV treatments increased tHAN concentration
- Repeated O_3 treatments had no effect on tHAN formation
- Repeated UV/O_3 treatments decreased tHAN formation

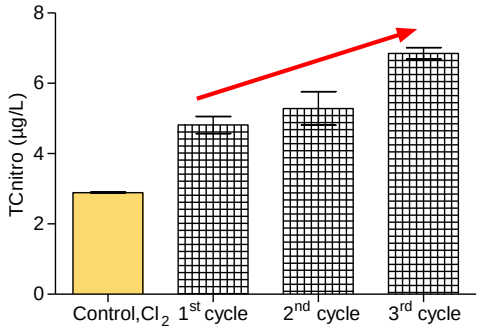
Trichloronitromethane

Single Treatments

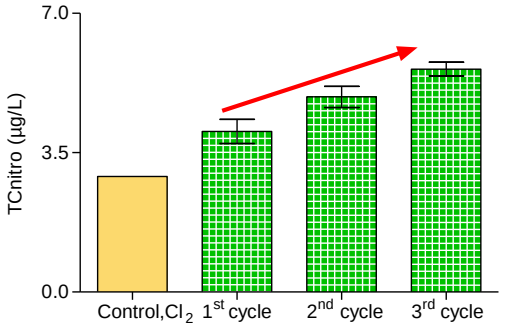


- Repeated UV treatments increased TCnitro concentration
- Repeated O_3 treatments increased TCnitro concentration
- Repeated UV/O_3 treatments decreased TCnitro conc.

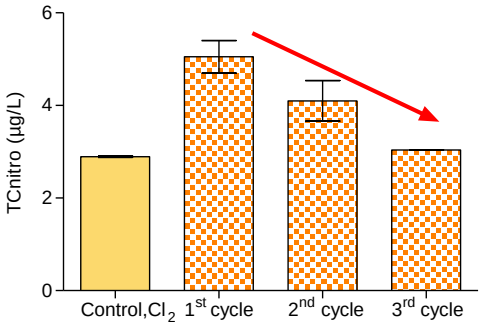
Repeated UV treatments



Repeated O3 treatments



Repeated UV/O3 treatments



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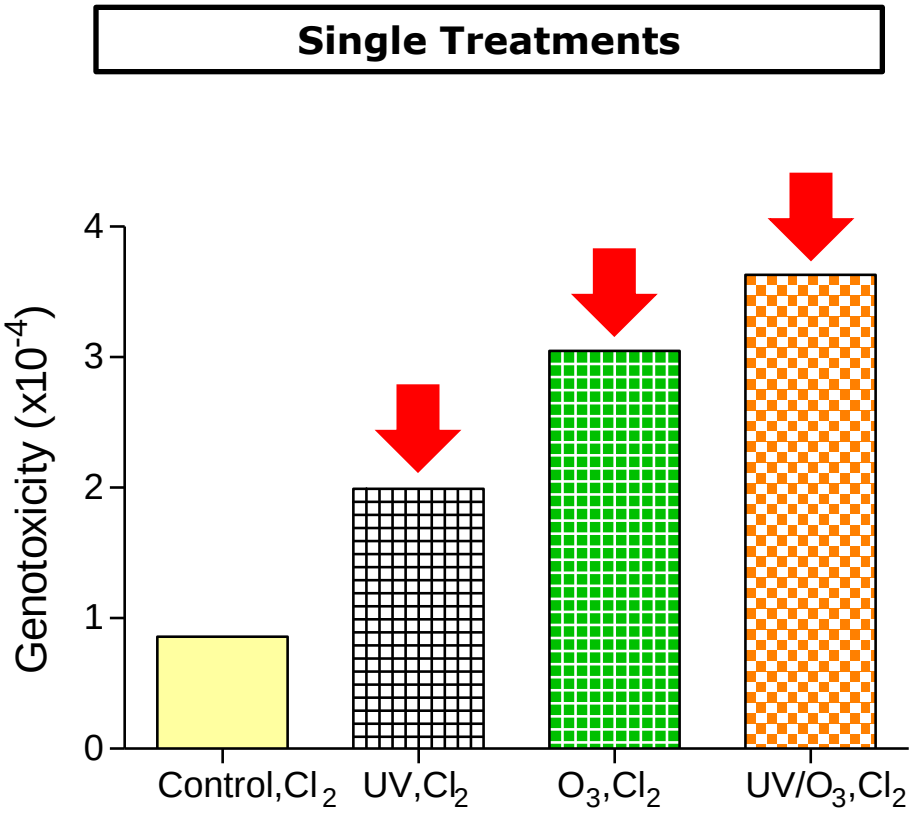
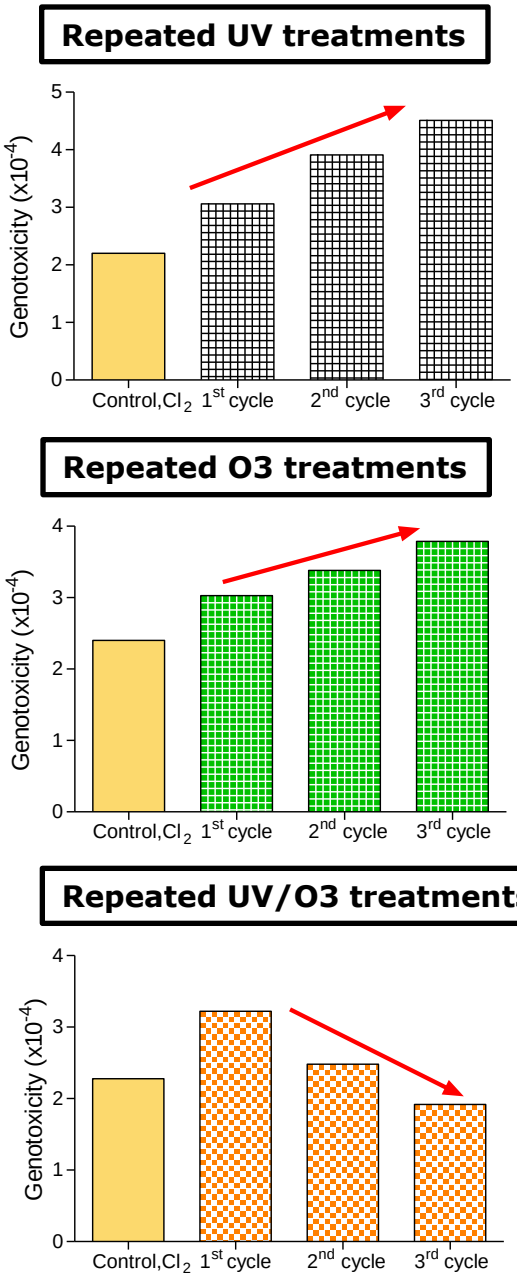
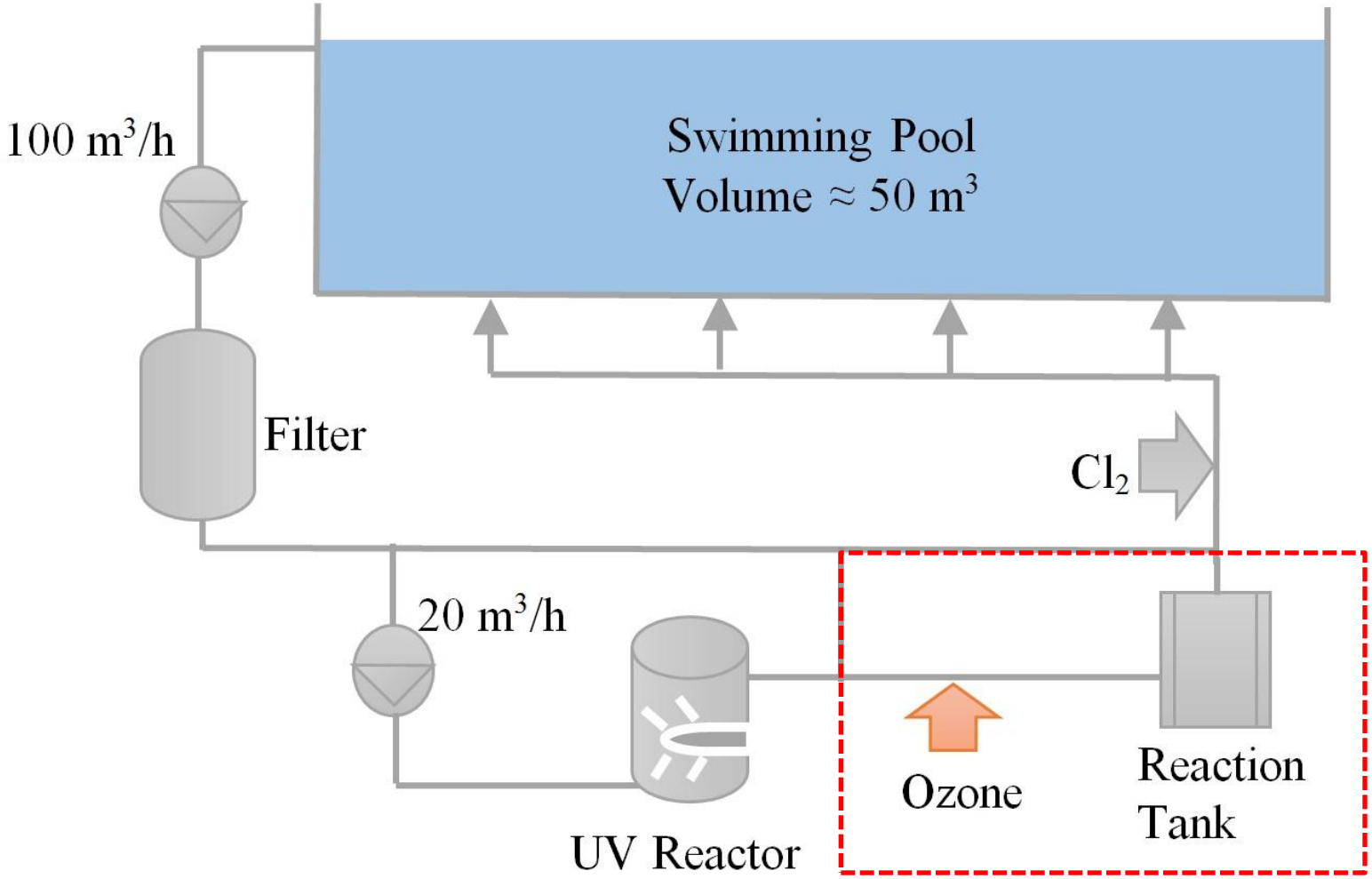
Predicted toxicity



- Repeated UV treatments increased toxicity
- Repeated O_3 treatments increased toxicity
- Repeated UV/O_3 treatments decreased toxicity



Gladsaxe muncipality pool



Thanks for your attention!